



## Short communication

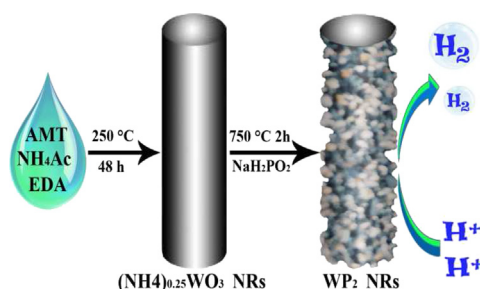
## Tungsten diphosphide nanorods as an efficient catalyst for electrochemical hydrogen evolution

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## HIGHLIGHTS

- A novel WP<sub>2</sub> nanorods catalyst with good crystallinity was successfully synthesized for HER catalyst.
- WP<sub>2</sub> nanorods demonstrate high activity towards hydrogen evolution reaction in wide pH media.
- WP<sub>2</sub> nanorods exhibit excellent stability for practical applications.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel tungsten diphosphide nanorods (WP<sub>2</sub> NRs) material with good crystallinity is synthesized as an efficient hydrogen evolution reaction (HER) electrocatalyst for the first time through phosphidation of (NH<sub>4</sub>)<sub>0.25</sub>WO<sub>3</sub> NRs precursor. Towards HER the WP<sub>2</sub> NRs exhibit an onset overpotential of 56 mV, a Tafel slope of 52 mV per decade and an exchange current density of 0.013 mA cm<sup>-2</sup> in acidic media. Further, the catalyst only needs overpotentials of 101 and 148 mV to deliver current densities of 2 and 10 mA cm<sup>-2</sup>, respectively. In particular, the catalyst can maintain its catalytic activity for 90 h at least, showing good long term operation stability. It also has excellent activity and stability under both neutral and basic conditions. The catalysis mechanism of WP<sub>2</sub> NRs is explored for the fundamental insights.

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## 1. Introduction

Hydrogen holds a great promise as a clean and sustainable fuel to replace the fossil ones [1–3]. Water electrolysis is a simple and promising way to mass-produce hydrogen [4,5]. In order to

improve hydrogen evolution reaction (HER) rate and lower the overpotential for reduction of energy consumption, a highly efficient electrocatalyst is required. Pt and Pt-based noble metals have been known as the best HER catalyst but their high expense and terrestrial scarcity significantly impede their practical applications. Proton exchange membrane-based electrolysis systems [6,7] and photocatalytic water-splitting devices [8] have been investigated under acidic conditions. Although abundant nickel based materials are active for HER [9–11], they suffer from poor stability resulting from corrosion in low pH media. Therefore, intensive researches are

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still carried out to design and synthesize efficient, acid-stable and non-noble-metal HER catalysts. Mo [12], Mo-based compounds including sulfides [13–21], carbides [22–25], selenides [26], borides [27] and nitrides [28,29] etc. as catalysts towards HER have been extensively investigated and greatly succeeded; nevertheless, their long term stability still needs further improvement.

Tungsten carbides share similar electronic configuration near the Fermi level with Pt [30], and show Pt-like behavior in surface catalysis [31]. They have been widely studied as efficient electrocatalysts for methanol oxidation and oxygen reduction [32,33]. They are also electrochemically active for the HER under acidic conditions but suffer from poor stability resulting from corrosion, especially at neutral and higher pH media [34]. Although  $W_2N$  nanowires exhibit improved stability towards HER, they need overpotential as high as 500 mV to attain a current density of  $10 \text{ mA cm}^{-2}$  [35].  $WS_2$  has attractive catalytic activity for HER in acidic media [36–41] but suffers from intrinsic poor electrical conductivity [42]. More recently, transition metal phosphides (TMPs) based on molybdenum and iron-group elements have been identified as active HER catalysts [43–51]. Tungsten phosphides (WP) have been intensively studied as catalysts for hydroprocessing (HPC), hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [52–54]. However, they have rarely been studied as HER electrocatalysts. Just very recently amorphous tungsten phosphide as HER catalyst is reported but the synthesis procedure involves several organic solvents and strict air-free conditions and thus is relatively difficult [55]. In addition, the catalytic behavior of tungsten phosphide in neutral and basic solutions has never been studied. Its long term stability also needs further improvement. In this work we demonstrate a facile approach to synthesize  $WP_2$  NRs with high crystallinity from  $(NH_4)_{0.25}WO_3$  NRs through phosphidation reaction. As a novel HER catalyst, it exhibits an onset overpotential of 56 mV, a Tafel slope of 52 mV per decade, an exchange current density of  $0.013 \text{ mA cm}^{-2}$ , and nearly 100% Faradaic efficiency (FE) in acidic media (pH 0.3). It only needs overpotentials of 101 and 148 mV to achieve current densities of 2 and  $10 \text{ mA cm}^{-2}$ , respectively. In particular, its catalytic activity can preserve for 90 h at least in acidic media and it is also highly active in either neutral (pH 7.0) or basic conditions (pH 14.0), rendering a great potential for practical applications.

## 2. Experimental

### 2.1. Materials

Ammonium metatungstate hydrate (AMT), Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma–Aldrich. Sodium hypophosphite ( $NaH_2PO_2$ ) was purchased from Aladdin Ltd. (Shanghai, China). Ethylenediamine (EDA), ammonium acetate ( $NH_4Ac$ ),  $H_2SO_4$  and other chemicals used were bought from Beijing Chemical Corporation. All reagents were used as received without further purification. The water used in all experiments was purified through a Millipore system.

### 2.2. Synthesis of $(NH_4)_{0.25}WO_3$ NRs

$(NH_4)_{0.25}WO_3$  NRs were prepared according to a reported method with modifications [56]. Briefly, 0.167 mmol AMT was dissolved in 20 mL of distilled water, followed by adding 18.0 mmol EDA and 10.0 mmol of  $NH_4Ac$ . After completely dissolving under magnetic stirring, the solution was transferred and sealed into a Teflon-lined autoclave with an internal volume of 50 mL, then heating to  $250^\circ\text{C}$  with a ramp of  $2.5^\circ\text{C min}^{-1}$  and keeping for 48 h in an electric oven. The green product was centrifuged and washed with distilled water and absolute alcohol several times,

respectively. Finally, the product was dried in a vacuum oven at  $60^\circ\text{C}$  for 24 h.

### 2.3. Synthesis of $WP_2$ NRs and bulk $WP_2$

To synthesize  $WP_2$  NRs, the as-prepared  $(NH_4)_{0.25}WO_3$  NRs and  $NaH_2PO_2$  with 1:20 in mole ratio of W/P were placed in two closed porcelain crucibles to heat up to  $750^\circ\text{C}$  with a ramp of  $5^\circ\text{C min}^{-1}$  and keep at this temperature for 2 h in Ar atmosphere, followed by cooling to ambient temperature naturally under Ar atmosphere. Bulk  $WP_2$  was synthesized by phosphidation of bulk  $WO_3$  with the same experimental conditions as  $WP_2$  NRs. The bulk  $WO_3$  was obtained by directly heating tungstic acid to  $500^\circ\text{C}$  in a muffle furnace for 4 h.

### 2.4. Characterizations

Powder XRD data were obtained by a RigakuD/MAX 2550 diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). SEM measurements were performed on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were carried out with a HITACHI H-8100 electron microscope (Hitachi, Tokyo, Japan) at an accelerating voltage of 200 kV. The BET surface area was measured with a Quantachrome NOVA 1000 system at liquid  $N_2$  temperature. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

### 2.5. Electrochemical measurements

All the electrochemical measurements were performed at room temperature with a CHI660E potentiostat (CH Instruments, China). A three-electrode setup with saturated calomel electrode (SCE), graphite plate and glassy carbon electrode (GCE,  $d = 4 \text{ mm}$ ) as reference, counter and working electrode, respectively was used. 0.5 M  $H_2SO_4$ , 1.0 M phosphate buffer and 1 M KOH solutions were used as electrolytes for measurements at pH values of 0.3, 7.0 and 14.0, respectively. In all measurements the SCE reference electrode was calibrated with respect to reversible hydrogen electrode RHE by adding a value of  $(0.242 + 0.059 \times \text{pH}) \text{ V}$ . Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range of 0.1–100 kHz at an overpotential of 200 mV and an AC potential amplitude of 5 mV.

## 3. Results and discussion

Fig. 1a shows the X-ray diffraction (XRD) patterns of  $(NH_4)_{0.25}WO_3$  NRs and  $WP_2$  NRs. The precursor shows characteristic diffraction peaks of  $(NH_4)_{0.25}WO_3$  (JCPDS No. 73-1084). After phosphidation process, all peaks in the measured XRD pattern can be attributed to the characteristic diffraction peaks of  $WP_2$  (JCPDS No. 35-1467) without any impurity peak observed. Fig. 1b and c show the scanning electron microscopy (SEM) images of  $(NH_4)_{0.25}WO_3$  NRs, clearly indicating the formation a large amount of one-dimensional (1D) nanostructures about 100 nm in diameter. It is noted that the phosphided products still maintain nanorod feature but with rough surface, which is clearly evidenced by their SEM (Fig. 1d and e) and transmission electron microscopy (TEM) images (Fig. 1f). The nitrogen adsorption/desorption isotherm plot shows that  $WP_2$  NRs have a Brunauer–Emmett–Teller (BET) specific surface area (SSA) of  $20.8 \text{ m}^2 \text{ g}^{-1}$  (Fig. S1a). The high-resolution TEM image (Fig. 1g) taken from a single rod reveals clear lattice fringes with interplanar distances of 0.423 and 0.287 nm corresponding to the (20-1) and (11-1) plane of  $WP_2$ , respectively. The selective area electron diffraction (SAED) pattern

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